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Measurements of optical refrigeration in ytterbium-doped crystals

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We measured anti-Stokes fluorescence cooling (optical refrigeration) in ytterbium-doped yttrium aluminum garnet (YAG). Pumping the 2.3% Yb³⁺:YAG crystal with 1.8 W of 1030 nm laser light produced a temperature drop of 8.9 °C from room temperature. The high thermal conductivity and ruggedness of this crystal make it an attractive material for use in optical refrigerators. Our spectral studies show that pure crystals of this material could be efficient for optical refrigeration at temperatures above ~ 100 K. Photothermal deflection measurements show that our current crystals can cool at ~ 250 K. Additionally, we measured optical refrigeration in a 5% Yb³⁺:Y₂SiO₅ crystal when pumped at 1050 nm. © 2001 American Institute of Physics. [DOI: 10.1063/1.1406544]

INTRODUCTION

The cooling of solids by anti-Stokes fluorescence or optical refrigeration has been an active area of experimental research since 1995.¹⁻⁹ The original demonstration of optical refrigeration¹ and much of the subsequent work^{2-5,9} was carwith ytterbium-doped fluoride glasses, ZrF₄-BaF₂-LaF₃-AlF₃-NaF (Yb³⁺:ZBLAN) or ZrF₄-BaF₂-LaF₃-AlF₃-NaF-PbF₂ (Yb³⁺:ZBLANP). Researchers have explored the potential of other ytterbium-doped glasses and crystals for optical refrigeration, and cooling has been measured in some of these materials by photothermal deflection techniques. 6,7,10 In ytterbium-doped optical refrigerants, the pump radiation is at an energy $h \nu \sim 1.24 \text{ eV} (\lambda \sim 1 \mu\text{m})$ and the fluorescence has an average energy a few kT higher. The resulting cooling efficiency $\sim kT/h\nu$ (heat lift/laser power) is a few percent at room temperature. Recently optical refrigeration has been measured in thulium-doped ZBLAN, a material that is pumped at $h\nu\sim0.7\,\mathrm{eV}~(\sim1.9~\mu\mathrm{m})$ and is nearly twice as efficient for cooling as the ytterbium-based optical refrigerants.8

Here we report on our studies of the optical refrigeration properties of ytterbium-doped YAG crystal (Yb³⁺:Y₃Al₅O₁₂) and on our initial measurements of optical refrigeration in Yb³⁺:Y₂Si₂O₅. This work is part of our ongoing program to search for improved materials for optical refrigeration. ¹⁰ The YAG crystals have physical properties such as high thermal conductivity and hardness that make it an attractive candidate for optical refrigeration. We measured the absorption and emission spectra for the Yb³⁺:YAG from 77 to 300 K and determine its potential optical refrigeration efficiency as a function of temperature. The predicted cooling efficiencies of Yb3+:YAG are almost as high as those for Yb3+:ZBLAN glass for T > 150 K. At lower temperatures the Yb³⁺:ZBLAN is predicted to cool much more efficiently. Our photothermal deflection measurements showed that our Yb³⁺:YAG crystals cool for temperatures above $\sim 250~\text{K}$ and that at room temperature they exhibit a cooling efficiency of $\sim 2\%$ when pumped at ~1030 nm. In bulk cooling experiments

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 Yb^{3+} :ZBLAN crystal cooled ~ 9 K below room temperature when a 1.6 W laser beam was passed through the crystal multiple times. The Yb^{3+} : $Y_2Si_2O_5$ crystal cooled a fraction of a degree in a single-pass experiment. As far as we know, these are the first demonstrations of net optical refrigeration in crystals; although Bowman and Mungan⁶ showed local cooling in crystals using photothermal deflection measurements.

PHYSICAL PROPERTIES

As an optical refrigerator host, YAG has several potential advantages over ZBLAN; see Table I. Since its thermal conductivity is more than 14 times that of ZBLAN, the temperature drop across a Yb3+:YAG cooling element will be at most a few degrees even when the cooler is operating at cooling powers of 1 W. Mechanically, YAG is much easier to work with. It is more durable and easier to polish than ZBLAN. The latter property is of practical importance because in some optical refrigerator designs high-reflectivity dielectric mirrors are deposited directly on the cooling elements. 11 On the negative side, YAG has some limitations as an optical refrigerator host. Its higher index of refraction increases the trapping of the fluorescence. The trapped fluorescence is reabsorbed and reemitted before escaping, thereby increasing the probability of nonradiative processes. Additionally, YAG has higher phonon energies than ZBLAN, which further increases the rate of nonradiative decay. 12 While these nonradiative decays are not a severe problem for cooling Yb³⁺:YAG, with its large 1.2 eV energy gap, it would be a problem for other rare-earth dopants. For example, optical refrigeration has been measured in Tm3+:ZBLAN, but nonradiative decays are expected to overwhelm optical refrigeration in Tm³⁺:YAG.

SPECTRAL STUDIES

We measured the absorption and emission spectra of Yb³⁺:YAG at temperatures of 77–300 K at roughly 10 K intervals. We used ultrahigh-purity crystals from Scientific Materials Corp. The spectra were taken with a CVI digicrom 240 monochromator equipped with a Santa Barbara Instru-

TABLE I. Physical properties of YAG and ZBLAN

	YAG	ZBLAN
Crystal structure	cubic	amorphous
Density (g cm ⁻³)	4.56	4.3
Thermal expansion (C^{-1})	7.8×10^{-6}	26.5×10^{-6}
Thermal conductivity (W m ⁻¹ C ⁻¹)	13	0.9
Refractive index	1.83	1.5

ment Group model ST-6 OPTO-HD charge coupled device. For the absorption measurements we used an Optronic Laboratories model 550 standard spectral radiance lamp.

Figure 1 shows the emission spectra, $\varepsilon(\lambda)$, the power per unit wavelength interval, for 1% Yb³⁺-doped YAG for several temperatures. The mean fluorescence wavelength λ_F ,

$$\lambda_F = \frac{\int \varepsilon(\lambda) \lambda d\lambda}{\int \varepsilon(\lambda) d\lambda},\tag{1}$$

is defined such that hc/λ_F is the average energy of the fluorescence photons. Figure 2 shows the mean fluorescence wavelength as a function of temperature. At lower temperatures λ_F shifts to longer wavelengths since the emission comes predominantly from the decay of the lowest levels of the excited manifold.

If the quantum efficiency is unity and there is no parasitic heating, the cooling efficiency is

$$\eta = \frac{\text{cooling power}}{\text{absorbed light}} = \frac{\lambda - \lambda_F}{\lambda_F}.$$
(2)

When the material is pumped with light of longer wavelengths, it cools, and when pumped at shorter wavelengths, it heats.

Figure 3 shows the absorption spectra $\alpha(\lambda)$ for 1% Yb³⁺-doped YAG for several temperatures. For optical refrigeration we need reliable determinations of the "cooling tail" of the absorption spectra (wavelengths longer than λ_F) However, it is difficult to directly measure $\alpha(\lambda)$ in this re-

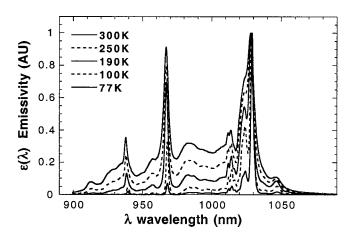


FIG. 1. Emission spectra for 1 wt % Yb^{3+} -doped YAG for several temperatures. All the spectra are normalized to unity at the peak near 1030 nm. The higher temperature curves are above the lower ones.

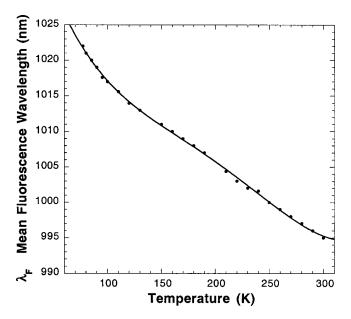


FIG. 2. The mean fluorescence wavelength for $1\%~Yb^{3+}$ -doped YAG vs temperature.

gion where it is significantly less than unity. To determine $\alpha(\lambda)$ in the cooling tail we employ the reciprocity relation, as in Ref. 10.

$$\alpha(\lambda) \propto \lambda^5 \varepsilon(\lambda) \exp[hc/\lambda kT].$$
 (3)

This relation gives the shape but not the amplitude of the absorption. From the direct absorption data, Fig. 3, we note that at around 933 nm the absorption coefficient α is approximately 0.5 cm⁻¹ for all the temperatures we measured. We therefore use this wavelength to normalize the reciprocity relation (3).

Figure 4 gives a comparison of the direct absorption measurements and the absorption coefficient obtained using the reciprocity relation. The difference in the two curves may be due to uncertainties in the background count rates and to reabsorption. At low absorption, α <0.03, background subtraction errors dominate the direct absorption measurements

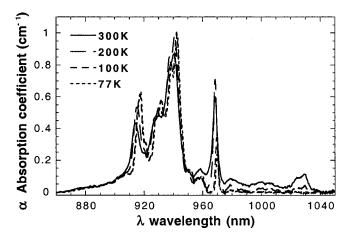


FIG. 3. Absorption spectra for 1% Yb³+-doped YAG for several temperatures. At wavelength 933 nm the absorption coefficient is $\sim\!0.5~\text{cm}^{-1}$ for all temperatures in the range studied; this fixed point is used for normalizing the reciprocity relationship shown in Figs. 4 and 5.

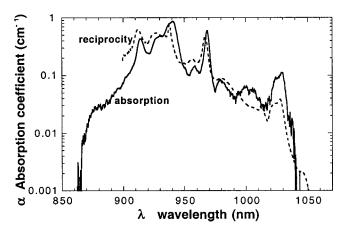


FIG. 4. Comparison of the absorption spectrum obtained with direct measurements and from the reciprocity relationship (dashed line) for a temperature of 300 K. The reciprocity curve is normalized to the absorption at 933 nm.

and the reciprocity relation is expected to be more reliable. At larger values of α , the reabsorption of the fluorescence distorts the shape of $\varepsilon(\lambda)$, so that direct absorption measurements are preferable.

For optical refrigeration, the most important region of the absorption spectrum is at long wavelengths, $\lambda > \lambda_F$. Figure 5 gives an expanded view of this region for several temperatures. The solid dot on each spectrum denotes the mean fluorescence wavelength for that temperature. The cooling tail is the region to the right of the each dot. In practical optical refrigerators, as described in Ref. 11, the reflectivity of the mirrors that trap the pump radiation limits the minimum useful absorption coefficient and, hence, the maximum pump wavelength. For current technologies, the useful range for the absorption coefficient is $\alpha = 10^{-4}$ to 10^{-3} cm⁻¹. The horizontal lines in Fig. 5 illustrate this range. From this figure, one can see how the cooling efficiency varies with temperature. For example, at 300 K an absorption coefficient of, say $\alpha = 3 \times 10^{-4} \text{ cm}^{-1}$, corresponds to a maximum pump wavelength of 1060 nm. Since the mean fluorescence wavelength at this temperature is $\lambda_F = 995 \text{ nm}$, Eq. (2) gives a

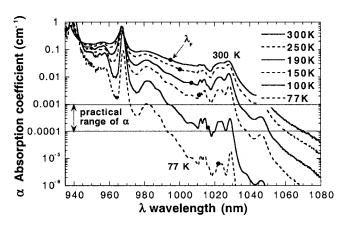


FIG. 5. The absorption at long wavelengths in 1% Yb³+-doped YAG for several temperatures as obtained from the reciprocity relation. The mean fluorescence wavelength λ_F is indicated by the dots on each curve. The useful range of the absorption coefficient for practical coolers is $\alpha \sim 10^{-3}$ to 10^{-4} cm⁻¹, as indicated.

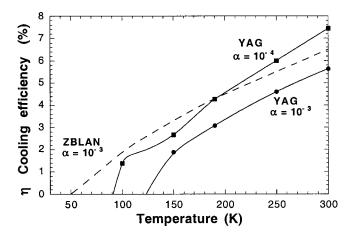


FIG. 6. The predicted cooling efficiencies (cooling power/laser power). The solid lines give the predicted results for ideal 1% Yb³⁺-doped YAG optical refrigerators that are pumped at an absorption coefficient of $\alpha = 10^{-3}$ or 10^{-4} cm⁻¹. The dashed line shows the predicted cooling efficiency for 1% Yb³⁺-doped ZBLAN from Ref. 10.

cooling efficiency η =6.5%. From Fig. 5 one can see that it will be difficult to have a Yb³⁺:YAG optical refrigerator that operates much below 100 K. At much lower temperatures, the maximum pump wavelength is shorter than the mean fluorescence wavelength so that the material will not cool.

The solid lines in Fig. 6 show the predicted cooling efficiencies (cooling power/laser power) in 1% Yb³⁺-doped YAG for pump wavelengths corresponding to $\alpha = 10^{-4}$ and 10^{-3} cm⁻¹. For comparison, the dashed line gives the predicted cooling efficiency for 1% Yb³⁺-doped ZBLAN for pump wavelengths corresponding to $\alpha = 10^{-3}$ cm⁻¹. Of Generally, the Yb³⁺:ZBLAN is predicted to have a higher cooling efficiency than the Yb³⁺:YAG.

PHOTOTHERMAL DEFLECTION MEASUREMENTS

We studied the cooling properties of Yb³⁺:YAG at room temperature and at lower temperatures using photothermal deflection techniques, as described in Refs. 1 and 3. A pump laser beam cools or heats a thin column of matter in the Yb³⁺:YAG crystal, changing its refractive index. The resulting thermal lens deflects a He:Ne probe beam. By chopping the pump beam and measuring the phase and amplitude of the deflection δ of the probe beam we determine the relative cooling and heating of the crystal. The amplitude of the deflection is proportional to the temperature change and hence to the cooling (or heating) power $P_{\rm cool}$ of the laser beam.

For small absorption, $\alpha L \leq 1$, where L is the length of the sample, the ratio of the cooling power P_{cool} to the pump power P_{pump} is

$$\frac{P_{\text{cool}}}{P_{\text{pump}}} = \alpha \left(\frac{\lambda - \lambda_F}{\lambda_F} \right) \text{QE} - \alpha (1 - \text{QE}) - \beta, \tag{4}$$

where a positive value represents cooling and a negative one is for heating. The first term is the anti-Stokes cooling ($\lambda > \lambda_F$) or Stokes heating ($\lambda < \lambda_F$) where QE is the quantum efficiency. The second term represent the heating from non-radiative decays, and the third term gives the background absorption separate from the absorption on the ytterbium

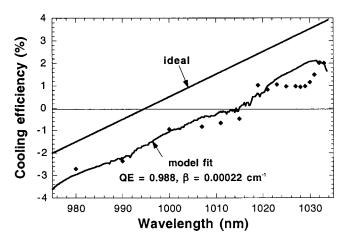


FIG. 7. The cooling efficiencies (cooling power/absorbed laser power) inferred from room temperature photothermal deflection measurements. Fitting the data gives the quantum efficiency QE=0.988 and background absorption β =0.000 22 cm⁻¹ and the proportionality constant between the deflection measurements and the cooling power. The straight line labeled "ideal" is the cooling efficiency for QE=1 and β =0.

ions; we take β to be independent of wavelength. By matching the photothermal deflection data for a 2.3% Yb³⁺:YAG crystal to Eq. (4), as shown in Fig. 7, we obtain the proportionality constant relating δ and $P_{\rm cool}$, the background absorption, and the quantum efficiency. The background absorption, β =0.000 22 cm⁻¹, may be due to low level contamination by transition metals, such as iron. The quantum efficiency is QE=0.988. The deviation QE from unity is likely due to fluorescence quenching by excitation transfers from excited ytterbium ions to other rare earth ions or the transition metals.

We performed photothermal deflection experiments at temperatures below room temperature. The sample was placed in a cryostat and maintained at temperatures between 200 and 294 K while the photothermal deflection signals were measured. Clear cooling signals were obtained for 252 K and higher temperatures. We could not observe cooling at lower temperatures.

BULK COOLING

To measure net optical refrigeration of Yb³⁺:YAG crystals at room temperature we used the experimental setup shown in Fig. 8. To minimize thermal conduction to the environment, the Yb3+:YAG crystal was set on the edges of cover slides in a vacuum chamber pumped to 10^{-6} Torr. The crystal was allowed to come to thermal equilibrium with the chamber and a reference picture was taken with a thermal infrared (IR) camera through a IR-transparent sodium chloride window on the vacuum chamber. The Ti:sapphire laser beam of 750 mW of pump light at 1030 nm was then directed through the crystal into a beam block outside the vacuum chamber. An IR picture was taken after 20 min and the difference between this image and the equilibrium reference image was produced. The chamber temperature is higher due to the absorbed fluorescence and the temperature of the crystal is lower. The IR intensity profile in Fig. 9 shows a difference of about ~0.36 K between the chamber

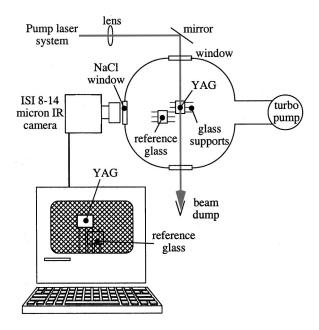


FIG. 8. Experimental setup for measuring bulk cooling. The laser source is a Spectra Physics model 171 argon ion laser pumping a Spectra Physics model 3900s cw Ti:sapphire laser. Temperature measurements were made with a pyroelectric thermal camera (ISI Group).

and the crystal. The results of similar measurements taken at 1020, 1025, 1030, 1040, and 1050 nm are shown in Fig. 10.

In the above experiment only about 10% of the laser light was absorbed in our sample at 1030 nm. To increase the absorbed pump power we placed a 2.3% Yb³⁺:YAG crystal inside an optical cavity created between two dielectric mirrors. This arrangement allowed us to get multiple passes of the laser through the sample so that most of the pump light is absorbed. With this method we were able to achieve 8.9 °C of cooling starting at room temperature.

We then had dielectric mirrors deposited on two opposite sides of several Yb³⁺:YAG crystals to create a monolithic cavity in each for trapping the pump radiation, as was done

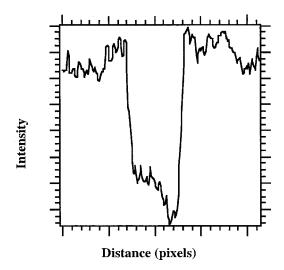


FIG. 9. Intensity profile of the infrared images of the Yb³⁺:YAG sample. A reference image was taken before the laser was turned on, and a second image was taken after 20 min of pumping. The curve shows the difference in brightness across the sample.

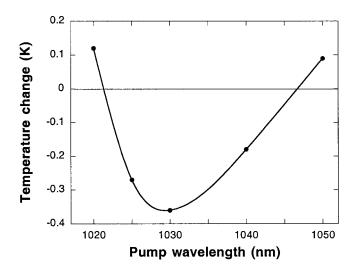


FIG. 10. The temperature changes for single-pass experiments. The dots give the temperature change of 1% Yb³⁺-doped YAG vs pump wavelength for 0.75 W of laser power. The curve is a smooth fit through the dots.

in Ref. 13 with Yb3+:ZBLAN. The pump light enters the crystal through a pin hole in one of the mirrors and is trapped by reflection from the dielectric mirrors and by total internal reflection from the sides of the crystal. While this approach was successful for the Yb³⁺:ZBLAN and ∼50 K of cooling from room temperature was measured, no cooling was seen for the mirrored Yb³⁺:YAG crystal. Two factors contribute to the lack of cooling, the increased fluorescence trapping in the crystal because of the presence of the mirrors and heating in the mirrors. When the two ends of the crystal are mirrored, the fluorescence has to escape through the other four faces. This reduces the escape probability for isotropic radiation to about one-third. This reduction of quantum efficiency is not sufficient to prevent the Yb3+:YAG crystal from cooling. However, if more than $\sim 10^{-4}$ of the light hitting the dielectric mirrors is thermalized on each reflection, the heating would overwhelm the anti-Stokes cooling.

In separate experiments we observed optical refrigeration in a 5% ytterbium-doped Y_2SiO_5 crystal. In a single pass

experiment, as described above, the infrared images showed that the Yb^{3+} : Y_2SiO_5 cooled about 1 K when pumped at 1050 nm. We have not carried out other cooling experiments with this material.

SUMMARY

We evaluated the potential of ytterbium-doped YAG crystals for use in optical refrigeration. We found that available materials are sufficiently pure and free of contaminants to optically cool at room temperature. Our studies of the absorption and emission spectra of Yb³⁺:YAG show that it should be an effective optical refrigerant to temperatures as low as 100 K. For comparable ytterbium doping, the cooling efficiency of Yb³⁺:YAG is not expected to be as high as that for Yb³⁺:ZBLAN, which is the most studied optical refrigeration material. Nevertheless, YAG has material properties that may make it a preferred cooling material for some uses. In particular, YAG has a much higher thermal conductivity than ZBLAN and its hardness and durability may make it easier to incorporate into practical devices.

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